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This report includes a brief summary of new techniques and advances in sample introduction for use in atomic spectrochemical analysis. Included in the review are new kinds of nebulizers, including the Babington system, the jet-impact nebulizer, and the fritted-disk unit. Also included are new arrangements for introducing solid samples into flames and plasmas. Finally, recent advances in understanding of sample transport mechanisms are discussed.

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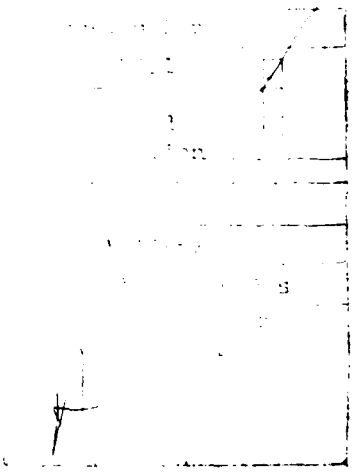
ADVANCES IN SAMPLE INTRODUCTION FOR ELEMENTAL ANALYSIS

by

Gary M. Hieftje



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Advances in Sample Introduction for Elemental Analysis

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In the recent past, atomic absorption spectroscopy has been the technique of choice for most elemental analyses. However, a relatively new addition to the analytical chemistry arsenal -- inductively coupled plasma spectroscopy -- is taking over many of the time-consuming analyses of samples in which the concentrations of several elements must be known. Unlike atomic absorption, inductively coupled plasma (ICP) spectroscopy is inherently a multi-element technique, since it relies on emission, and instrumentation used in the ICP method is ordinarily configured to exploit this capability.

Unfortunately, the ICP technique suffers from some of the same problems that have long plagued atomic absorption, especially those revolving around sample introduction. Ordinarily, sample introduction methods for either AA or ICP use are designed to handle only solution samples, requiring that other kinds be ashed, digested, or pre-treated in some other way. Moreover, once the samples are in a solution form, they are largely wasted because of the relative inefficiency of most sample introduction approaches. Finally, because solutions are ordinarily introduced into an ICP or AA instrument in the form of an aerosol, a spraying technique must be employed which is usually dependent on gas flow; often, such gas flows are not entirely compatible with plasma or flame operation.

Importantly, all these deficiencies are being examined in detail at the present time. Methods are being sought which would enable the direct

introduction of solid samples into flames or plasmas used in AA or ICP methods, respectively. Also, more efficient systems are being designed for the introduction of solution samples. Many of these new systems require lower gas flows than former ones and operate with greater efficiency. Finally, a number of workers are seeking to elucidate the fundamental processes by which sample sprays are converted to free atoms which can then be used for emission or absorption analyses. In this brief article, a number of these advances will be outlined.

In the area of solid-sample analysis, some of the most exciting work is being carried on at the University of Alberta by the research group of Dr. Gary Horlick. In these studies, two different methods are being examined. In one approach, laser vaporization of solid samples is being exploited to enable the resulting vapor to be swept conveniently into a flame or plasma. A specially designed chamber, placed below an ICP torch or atomic absorption flame, is equipped with a transparent window through which high-power laser pulses can be sent. The sample to be examined is then placed within this chamber and irradiated with one or more laser pulses, to generate sample vapor which is carried by a flowing gas stream into the flame or plasma. In a variant on this scheme, the same group has attempted the analysis of powders by attaching a double-sided sticky tape to a carbon rod. The tape is then rolled in the powder of interest and located in the sample chamber where laser irradiation can take place. To date, only ruby lasers have been employed in this method, although it is anticipated that carbon dioxide lasers would also be useful.

The other method being examined by the Horlick group has been dubbed "direct sample insertion". More easily automated, this latter technique

involves the placement of a powdered sample into an electrode similar to those commonly used in dc arc or high-voltage spark spectroscopy. This packed electrode is then injected automatically by means of a pneumatic system into the region in an ICP torch ordinarily occupied by the plasma. The radio-frequency power otherwise used to sustain the plasma then inductively heats the graphite sample electrode, causing it to emit sufficient electrons to ignite the plasma. At this point, sample material begins volatilizing from the electrode directly into the plasma. The method would appear to be potentially very valuable for routine analyses.

One of the most attractive new methods for producing sample sprays involves the so-called "Babington" nebulizer. In this nebulizer, solutions to be sprayed are not forced to flow through a small orifice, as in most competitive devices. Instead, the solution need only flow past an orifice, out of which issues a high-velocity jet of gas. The liquid is thereby efficiently disrupted into a spray of tiny droplets, which can be sent into a flame or plasma. Importantly, the Babington nebulizer is relatively immune from clogging problems and has been shown to be capable of producing sprays from highly viscous samples or those which contain particulate material.

Another advance in sample spraying involves the use of a fritted disk. Being pursued by a number of workers, the fritted-disk nebulizer involves the use of a sintered glass device, similar to those used in gas-dispersion tubes. Samples to be sprayed are simply dropped or flowed across the surface of the fritted glass disk, with an appropriate gas being directed through the disk itself. The resulting sample spray has been found to contain extremely small and homogeneous droplet sizes and to be produced with extremely high efficiency. In recent tests, it has been shown that nearly 100% of the nebulized solution can be directed to a flame or plasma.

Two other new methods for sample introduction in atomic spectroscopy are being pursued in our own labs at Indiana University. In one approach, microliter-sized samples can be dispensed under direct digital control into a microfurnace of the kind ordinarily used for atomic absorption. In this method, a tiny glass needle is repetitively inserted into and withdrawn from the microliter quantity of solution, withdrawing from it micro-aliquots of the same liquid. Ordinarily, such micro-aliquots have a volume of approximately one nanoliter. Accordingly, each micro-aliquot can be treated as an individual sample, so that large numbers of them can be repetitively dispensed into a carbon furnace, thereby improving precision. Also, because the aliquots are extremely small, they can be directed onto a hot carbon surface and thereby produce unusually small, dried crystals. Small crystals serve to reduce commonly observed interferences caused by occlusion of the sought-for substance in a sample matrix. Finally, repetitive dispensing of the nanoliter volumes enables samples to be pre-concentrated on the carbon surface to enhance sensitivity.

In another new technique, we are exploring the use of a "jet-impact" nebulizer. This new device involves forcing the sample solution of interest through a relatively small orifice, formed from a watch jewel. The resulting jet is then directed against a solid surface; when the jet velocity is great enough and travels a sufficient distance before striking the surface, it is disrupted efficiently into tiny droplets which can be directed into a flame or plasma. Importantly, the new device is relatively easy to automate, can use microliter sample volumes, and requires no gas flow for production of an aerosol.

An interesting series of studies utilizing a tandem nebulizer arrangement is being carried out at the Cincinnati laboratories of the Environmental Protection Agency, by K. A. Wolnik and F. L. Fricke. In these experiments, the solution to be analyzed is sprayed first by a conventional concentric nebulizer of the "Meinhard" type. The resulting aerosol is then fed into a second nebulizer, of the "cross-flow" kind. Also sent into the second nebulizer is a solution whose intereaction with the sample is desired. For example, internal standard species can be added in this way, complexing agents can be introduced, or internal standards can be combined with a sample. The resulting signals give the appearance of those in which the two different solutions had earlier been mixed. However, it has been found possible by the Cincinnati workers even to combine ordinarily immiscible liquids, enabling entirely new kinds of studies and analyses to be performed. The system would also seem to be extremely valuable for automating established procedures.

Other important advances in the area of sample introduction methods for atomic spectroscopy revolve around an examination of processes occurring during the spraying process or when sample aerosols are transported between a sprayer and the flame or plasma in which they are atomized. Important studies being carried out by the research group of Dr. R. F. Browner at Georgia Institute of Technology have shown that many of the processes involved in spraying are not well understood and can lead to serious analytical errors. For example, they have shown that the tiniest droplets of an aerosol often contain much higher concentrations of a dissolved solute than were present in the original bulk solution. These findings have been corroborated by work carried out at Colorado State University under the direction of Dr.

R. K. Skogerboe. Similarly, the Browner group has shown that the transport of aerosol through typical spray chambers used in AA or ICP work can exacerbate these problems. Because many different designs for spray chambers exist, and because most discriminate against large droplets to a certain extent, the enhancement effects in small droplets might be more or less pronounced depending upon the particular apparatus being employed.

Importantly, most practitioners of atomic spectroscopy have now recognized that sample introduction techniques are often the bottleneck to accuracy and precision in routine analytical situations. Work is continuing not only in the investigations described above, but in others, with a view toward providing new techniques and procedures that are both simple to implement and automate, and which produce results of high reliability.

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